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SALIENT FEATURES OF INFRARED SPECTRAL ANALYSIS OF A GLASS-FORMING BATCH CONTAINING BORIC AND SILICIC ACIDS

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The results of IR spectroscopy of boric and silicic acids, which are the main components of the batch for fabricating microspheres, are presented. It is proved that the structure of boric and silicic acids contain water in molecular form (crystal-hydrate) and as OH groups, respectively. A formula is given for calculating the absolute degree to which the bands differ with respect to wave number and intensity. It is shown that half of the spectral bands of both acids can be used only conditionally to identify the acids, and almost a third of these bands are the main (strongest) bands. The bands at 1195 cm^{-1} in the spectrum of boric acid and 1180 and 1200 cm^{-1} in the spectrum of silicic acid are indistinguishable with respect to position and intensity and cannot be used for analysis. The wave number is a necessary and sufficient indicator for identifying the acids in the mix, but in the case of the conditionally used bands analysis of a mixture of acids is impossible if their intensity is neglected.

The alkali borosilicate system is widely used for developing commercial compositions and in research work [1–3], but it is impossible to conduct technological work without the requisite analytical studies. IR spectroscopy is a method of physical-chemical analysis that enables diagnostics of compounds by bond type. Its virtue is that IR radiation acting on atomic groups does not change the physical state and the chemical composition of the objects being investigated. IR spectra are formed by transitions between the vibrational levels of molecules (atoms) in the electronic ground state. The structure, position, intensity, and polarization of the bands make it possible to obtain data on the structure of substances and crystal-chemical modifications and to monitor the course of solid-phase reactions. To obtain spectra 0.01 – 0.10 g of substances containing light atoms, which cannot be determined by, for example, x-ray methods, are sufficient. A specific feature of glass analysis is that the structure and properties of glass that depend on the impurity composition and the heating history change in time and corresponding changes occur in the IR spectrum.

Even though IR spectroscopy offers great possibilities, the available analytical data for the alkali borosilicate system are very limited and cannot be used to judge whether or not a borosilicate motif has formed or the structure of the synthesized material consists of mutually isolated borate and silicate fragments or these components are all present simultaneously. The system indicated was studied in this connection.

This article presents results concerning the IR spectroscopy of orthoboric (in what follows — boric) and silicic acids,² by means of which the glass forming compounds B_2O_3 and SiO_2 are introduced into the batch for producing microspheres [3].

The spectra of the acids — analytical grade boric acid H_3BO_3 and ultrapure-grade silicic acid $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ — were recorded in the range 4000 – 400 cm^{-1} with resolution 4 – 8 cm^{-1} (Fig. 1, Table 1). “Sartogosm” analytical balances were used to obtain $0.01\text{ g} \pm 0.02\text{ mg}$ of the experimental substances which amount was mixed with 0.3 g potassium bromide. The mixtures were milled for 1 min in a vibrational mill with ShKh15 steel spherical milling bodies (GOST 801–78). Next, they were placed separately into a sample holder and then into a module of a NEXUS diffuse reflection

² A. Sh. Komarevskaya (deceased), a colleague at the Russian Federal Nuclear Center – All-Russia Scientific-Research Institute of Experimental Physics, provided the IR-spectroscopic data.

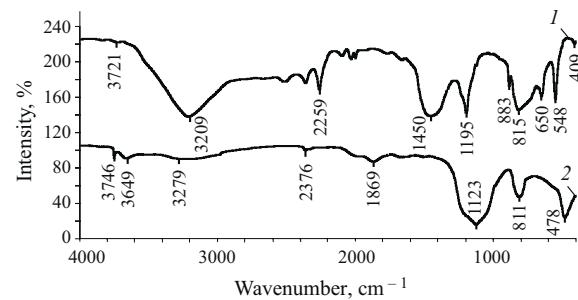


Fig. 1. IR spectra of boric (1) and silicic (2) acids.

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TABLE 1.

Position of the band maximum, cm ⁻¹ /band intensity, %		Position of the band maximum, cm ⁻¹ /band intensity, %	
H ₃ BO ₃	SiO ₂ · nH ₂ O	H ₃ BO ₃	SiO ₂ · nH ₂ O
409/3	—	—	1264/61
418/7	—	1285/88	—
—	420/70	—	1293/30
462/1	—	—	1350/23
—	478/91	1450/100	—
—	524/61	—	1507/16
548/80	—	1662/28	—
—	550/56	—	1750/14
—	566/53	1763/18	—
599/35	—	—	1804/16
650/75	—	—	1869/21
676/66	—	1927/15	—
—	679/40	—	1937/14
—	729/42	—	1992/14
746/82	—	1998/23	—
—	764/44	2029/26	—
—	811/67	2095/22	—
815/93	—	—	—
883/61	—	2259/66	2264/3
938/28	—	2359/58	2371/2
—	989/51	—	2376/3
1015/21	—	—	—
—	1034/82	2514/55	—
—	1050/88	2677/52	3198/17
1062/21	—	2950/62	—
—	1086/95	—	—
1119/56	—	3209/100	3649/17
—	1123/100	3500/34	3668/16
—	1143/96	—	—
—	1180/91	—	3746/16
1195/96	—	3721/4	—
—	1200/88	—	3746/16
1230/75	—	3829/2	—

IR-Fourier spectrometer. In addition, x-ray analysis of both acids was performed (using a DRON-3M diffractometer with CuK_α radiation) and the composition of the silicic acid was determined gravimetrically.

A comparative analysis revealed certain differences and signs of similarity between the IR spectra of boric and silicic acids and their structures. In both cases the presence of shoulders in the region 2600 – 400 cm⁻¹ and asymmetric contours of the main (strongest) bands indicated a complicated structure of the spectra which is due to a superposition of a number of bands. With a few exceptions the bands in the spectrum of boric acid are stronger than those of silicic acid. The bands of boric acid are narrow with sharp peaks and are

well-resolved in contrast to the diffuse bands of silicic acid. In the region 2600 – 400 cm⁻¹ the main (strongest) bands of boric acid are shifted in the direction of short wavelengths. These are indications of a crystalline structure for boric acid and an amorphous structure for silicic acid.

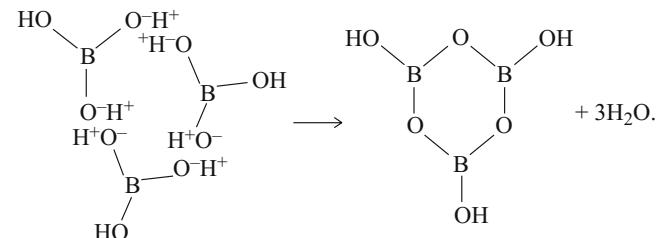
The diffuse band with average intensity at 3198 cm⁻¹ in the spectrum of silicic acid and the intense band (100%) at 3209 cm⁻¹ of boric acid attest to the presence of water but, evidently, in different forms. They were identified as follows.

In the spectrum of boric acid, the intensities of the bands of the stretching vibrations of water at 3209 cm⁻¹ and the stretching vibrations of the structure-forming group [BO₃] at 1450 cm⁻¹ [4] equal 100%. The clarity of the contours of the bands due to water in boric acid — stretching and bending vibrational ($\delta_{\text{H}_2\text{O}}$ at 1662 cm⁻¹) — should be noted; this is characteristic for structure-forming components.

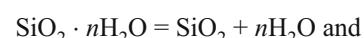
In the spectra of the acids, the stretching and bending vibrational bands have the same shape, but the intensity of both types of bands is the same for silicic acid whereas the bending vibrational band of water in boric acid is three times weaker than the stretching vibrational band, i.e., the water in boric acid is not a factor in the structural amorphization of the acid. The band at 3500 cm⁻¹ indicates “coupled” (structure-forming) OH groups, and resonance bonds can form because of the closeness of these groups to one another [5]. Subsequently, this probably resulted in the formation of boroxol rings — the main motifs of the borate structure. The “coupled” OH groups are found even in glass which is obtained by removing water from boric acid [4]. Conversely, the molecular water in the structure is not bound, wedges apart fragments of the structure, and forms cracks [6], i.e., it amorphizes the structure.

The scheme for the formation of the ring structural motif of boric acid with the participation of resonance bonds is as follows:

The energies required to break the bonds with molecular



water being released in dehydration reactions



are 4.66 ± 0.23 and 54.7 ± 3.0 kcal/mole [7, 8], respectively. The order of magnitude difference also gives a basis for assuming that the water is strongly bound in the structure of boric acid and cannot be present in a molecular form, and the low energy of dehydration of silicic acid indicates the oppo-

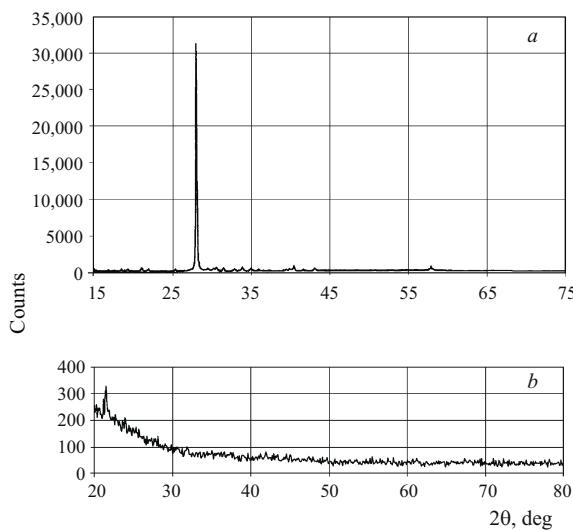


Fig. 2. Diffraction patterns of boric (a) and silicic (b) acids.

site. X-ray phase analysis confirmed that the structure of boric acid is crystalline and that of silicic acid is amorphous (Fig. 2).³

The well-known methods of [9, 10]⁴ showed that the mass ratio (%) in the reagent "silicic acid" is $\text{SiO}_2 : \text{H}_2\text{O} = 80 : 20$ (the theoretical ratio is 77 : 23, but calcination mass losses 20 – 28% are admissible). So, water in the form of OH groups (hydroxyl form) is present in the structure of boric acid, and molecular water in amounts no greater than one molecule is present in the structure of silicic acid.

Half the bands in the spectra of the acids had the same or almost the same wave number position ν or intensity I (see Figs. 1 and 3). We shall call them critical. This determined the specific nature and basic difficulty of identifying boric and silicic acids by means of IR spectroscopy when they are present simultaneously in the glass-forming batch. This fact is not mentioned in the literature, and we believe that our experimental data could be of interest to the appropriate specialists.

For the critical bands, we determined the absolute degree of difference Δ (%), Table 2) in the parameters ν and I (Δ_ν , Δ_I) according to the general formula

$$\Delta = \left| 100 - \frac{100 p_{\min}}{p_{\max}} \right|,$$

where p_{\min} and p_{\max} are the smallest and largest of the parameters of the bands being compared.

³ N. L. Zolotukhina and É. G. Ryabov, colleagues at the Russian Federal Nuclear Center – All-Russia Scientific-Research Institute of Experimental Physics, performed the x-ray phase analysis.

⁴ E. G. Orlikova and I. V. Astakhova, colleagues at the Russian Federal Nuclear Center – All-Russia Scientific-Research Institute of Experimental Physics, performed the analysis using the method of [9]. E. F. Medvedev used the method of [10] to perform the analysis.

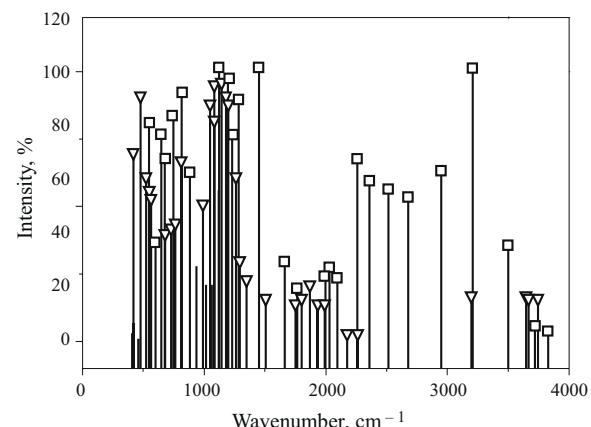


Fig. 3. Line spectrum of boric (□) and silicic (▽) acids.

We agreed that if $\Delta \leq 10\%$ for both parameters (ν and I), then the bands are indistinguishable and unusable for identifying boric and silicic acids when both are present simultaneously in the batch. If $\Delta > 10\%$ for at least one parameter, then the bands can be used conditionally. If $\Delta > 10\%$ for both parameters, then the bands can be used unconditionally for IR analysis of the substances present in the batch. In our present work all bands except the critical ones were consid-

TABLE 2.

H_3BO_3	$n\text{SiO}_2 \cdot \text{H}_2\text{O}$	Δ_ν	Δ_I	Absolute degree of difference, %		Applicability for the analysis
				H_3BO_3	$n\text{SiO}_2 \cdot \text{H}_2\text{O}$	
418/7	420/70	0.5	30	–	+	v
548/80	550/56	0.4	30	–	+	v
676/66	679/40	0.4	39	–	+	v
815/93	811/67	0.5	28	–	+	v
1062/21	1050/88	1.1	76	–	+	v
1119/56	1123/100	0.4	44	–	+	v
1195/96	1180/91	1.3	5	–	–	v, I
1195/96	1200/88	0.4	8	–	–	v, I
1230/75	1200/88	2.4	15	–	+	v
1230/75	1264/61	2.7	19	–	+	v
1285/88	1264/61	1.6	31	–	+	v
1285/88	1293/30	0.6	66	–	+	v
1662/28	1653/16	0.5	43	–	+	v
1763/18	1750/14	0.7	22	–	+	v
1927/15	1937/14	0.5	7	–	–	v, I
1998/23	1992/14	0.3	39	–	+	v
2259/66	2264/3	0.2	95	–	+	v
3209/100	3198/17	0.3	83	–	+	v

dered to be of the latter type. Examples of the use of the formula for finding Δ in practice are given below.

Example 1. The bands at 548 cm^{-1} ($I = 80\%$) and 550 cm^{-1} ($I = 56\%$) in the spectrum of boric and silicic acids were chosen from the critical group. Here we have $548 < 550$ but $80 > 56$. Thus,

$$\Delta_v = \left| 100 - \frac{100 \times 548}{550} \right| = 0.4\% < 10\%,$$

so that the bands are indistinguishable with respect to the parameter v and are unsuitable for identifying the substances in the batch;

$$\Delta_I = \left| 100 - \frac{100 \times 56}{80} \right| = 30\% > 10\%,$$

so that the bands are distinguishable with respect to the parameter I and can be used to identify the substances in the batch.

Final conclusion: the pair of bands being compared is conditionally applicable to analysis.

Example 2. Let us compare the bands at 1195 cm^{-1} ($I = 96\%$) and 1180 cm^{-1} ($I = 91\%$) which belong to the spectra of boric and silicic acids, respectively. We have $1195 > 1180$ and $96 > 91$. Hence

$$\Delta_v = \left| 100 - \frac{100 \times 1180}{1195} \right| = 1.3\% < 10\%,$$

so that the bands are indistinguishable with respect to the parameter v and are unsuitable for identifying the substances in the batch;

$$\Delta_I = \left| 100 - \frac{100 \times 91}{96} \right| = 5\% < 10\%,$$

so that the bands are also indistinguishable with respect to the parameter I and are unsuitable for identifying the substances in the mixture.

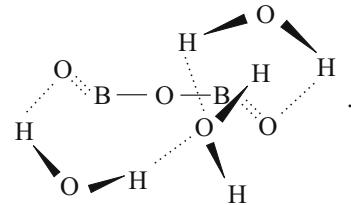
Final conclusion: the pair of bands being compared is inapplicable for analysis.

We note that the wave number was the determining parameter for analyzing the IR spectroscopic data. After closely spaced bands are found in the spectrum of a mixture of substances to be identified, it is necessary to calculate the absolute degree of difference Δ_v . The wave number is a necessary and sufficient band indicator, while the intensity is a necessary (as a rule it is not given in the literature) but not sufficient indicator. For example, the bands with maxima at 1119 and 550 cm^{-1} in the spectra of boric and silicic acids (see Fig. 1 and Table 1), respectively, have the same intensity — 56% , but it is completely obvious that there is no point in comparing them.

The experimentally established fact the IR spectra of boric and silicic acids are similar is mostly likely due to the closeness of the structures of these substances.

The structural network of boric acid is a triclinic layered structure based on a planar triangle $[\text{BO}_3]$. The triangular groups are intercoupled by hydrogen bonds, where the bond lengths are $l_{\text{B}-\text{O}} = 0.58 \text{ \AA}$ and $l_{\text{O...O}} = 2.72 \text{ \AA}$; the OH...O bonds are linear [11]. At the same time, boric acid is represented in [12, 13] in the crystalline form $\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, but then the formation of boroxol rings cannot be explained. Actually, the structure of $\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ can be represented in only one way — two water molecules forming hydrogen bonds (shown as a linear succession of dots) with B_2O_3 as the base, and a third molecule unites the first two to form a distinctive ring.

The hypothetical structural scheme of the crystal hydrate $\text{B}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ is



It is unlikely that the complex structure of the crystal hydrate “boric acid” was stable for a long time, though this form is used to calculate the batch under the assumption that heat treatment removes all water [13]. It has been established experimentally that some water remains [4], and this can only be the structurally bound water in the form of OH groups (see above). Consequently, the structural motif of the acid must be represented as a triangle $\text{B}(\text{OH})_3$ with a boron atom at the center and OH groups at the vertices.

The data on the structure of silicic acid itself are quite sparse; its salts (silicates) have been investigated in greater detail. This information was used to explain the structure of the acid. In [11] it is indicated that the tetrahedron $[\text{SiO}_2(\text{OH})_2]$ comprises the base of the triclinic structure of alkali silicates (they are synthesized as components of the batch for microspheres [3]). With coupling at the vertices and the formation of hydrogen bridges the tetrahedral form different types of chains which molecular water joins into layers. On the one hand the formation of resonance bonds $[\text{O}_2\text{Si}-(\text{OH})_2] \uparrow \downarrow [\text{(OH})_2-\text{SiO}_2]$ with water being released explains well the possibility of a network of $[\text{SiO}_4]$ tetrahedral forming. At the same time the variable water content in the reagent “silicic acid” (in our case it has been proven that one molecule is present) does not permit representing the molecular formula in the classical variant — H_2SiO_3 .

A tetrahedron differs from a triangle only by one vertex, but the additional degree of freedom engenders a large variety of structure motifs (six of these are presented in [11]), which can coexist simultaneously in the network of a substance and thereby amorphize its structure. Conversely, the manner in which the triangles are coupled together limits the structural variety, so that boric acid cannot be classified as an amorphous substance. The features that both acids have in

common are triclinicity and the two-dimensionality. This is most likely largely responsible for the fact that the IR spectra of the acids are identical with respect to the arrangement of the bonds, but their differences with respect to intensity and shape (stronger and sharper peaks are observed in the spectrum of boric acid) indicated a higher degree of ordering (crystallinity) of boric acid and amorphousness of silicic acid.

So, the structures of boric and silicic acids are largely identical and contain water in different forms — hydroxyl and molecular, respectively. To identify boric and silicic acids in the batch mix by means of IR spectroscopy the bands with maxima at 1195 cm^{-1} of boric acid and 1180 and 1200 cm^{-1} of silicic acid must be excluded from the analytical bands because they are indistinguishable with respect to spectral position and intensity. Almost half of the bands can be regarded as only conditionally suitable for analysis, and among these bands almost 30% comprise the main spectral bands (these are the strongest bands, are well-resolved, and easily determined as components of complicated contours).

One additional indicator must be given for the critical bands in addition to the wave number — the intensity. The bands⁵ with maxima at 409 (3), 462 (1), 599 (35), 650 (75), 746 (82), 883 (61), 938 (28), 1015 (21), 1450 (100), 1577 (38), 2020 (26), 2095 (66), 2359 (58), 2514 (55), 2677 (52), 2950 (62), 3500 (34), 3721 (4), and 2839 (2) cm^{-1} belong to the spectrum of boric acid and do not have any close analogs in the spectrum of silicic acid. The latter can be identified in the batch on the basis of bands with maxima at 478 (91), 524 (61), 566 (53), 729 (4), 764 (44), 989 (51), 1034 (82), 1086 (95), 1143 (96), 1350 (23), 1507 (16), 1804 (16), 1869 (21), 2176 (3), 3649 (17), 3668 (16), and 3746 (16) cm^{-1} .

⁵ The band intensities (%) are given in the parentheses.

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